Bulk and Bioavailable Heavy Metals (Cd, Cu, Pb, and Zn) in Surface Sediments from Mazatlán Harbor (SE Gulf of California)

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Abstract This work evaluates current metal concentrations (Cd, Cu, Pb and Zn) and the operational bio-available chemical extraction fraction in surface sediments in Mazatlán Harbor in Northwest México. Sediment samples were also analyzed for organic carbon, carbonates and particle size. Ranges of bulk metal were as follows: Cd from 3.1 to 3.3 µg/g, Cu from 31.9 to 44.9 µg/g, Pb from 49.6 to 54.0 µg/g, and Zn from 217.8 to 323.5 µg/g. In terms of biological effects, metals concentrations in the sediments lie between the low and median ranges of the mean quality guideline criteria. Comparatively, the metals concentrations increased from 1983 to 1994 and then for 2006, except Pb and Cd that decreased in the last period of time. The bio-available fraction of metals increased from 1983 to 1994, but only bio-available Cu increased from 1994 to 2006, due to mobilization of this metal from the organic matter–sulfide phase.

Keywords Surface sediment · Heavy metals · Enrichment factor · Bio-available fraction

Metals arrive at coastal lagoons from a variety of natural and anthropogenic sources. Most of the metals reaching the coastal zone are accumulated mainly in bottom sediments.

Because metals are some of the most persistent contaminants in the environment, they may progressively accumulate in sediments. The mobility of metals from sediments to the water column and their consequent bio-availability and toxicity to marine life depends on their geochemical partitioning (Tessier et al. 1979; Luoma 1989). Thus, knowledge of this process is of critical importance in assessing the harmful potential of metals in aquatic environments.

Mazatlán Harbor is located in Northwest México, in the Pacific coast along the SE Gulf of California, within a coastal lagoon system known as "Estero de Urías". Studies on heavy metals in sediments carried out in the middle-1980's reported natural levels in most of the sites sampled in the coastal lagoon (Osuna-López et al. 1986). One decade later, anthropogenic activities mainly related to untreated domestic effluents, leaded gasoline combustion, the naval industry, and coal-burning electricity production had enriched concentrations of Cd, Cu, Pb and Zn above the background levels (Soto-Jiménez and Páez-Osuna 2001). The present study evaluates current metal concentrations and the operational bio-available chemical extraction fraction in surface sediments in the lagoon system.

Materials and Methods

Forty surface sediment samples were collected using a plastic tube (ID = 7 cm) from four sites in the lagoon system in the dry and rainy seasons of 2006 (Fig. 1). The sites in the lagoon were selected considering their biological diversity and proximity to human activities. The sites receive inputs from land runoff during the rainy season from July to October. Mangroves are present on the

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margins (*Rhizophora mangle*, *Laguncularia racemosa* and *Avicennia germinans*). Site A receives effluents from a semi-intensive shrimp farm, sites B and C do not receive any direct discharge and site D receive discharges from the thermoelectric plant.

Sediments were analyzed for organic carbon (Loring and Rantala 1992), carbonates (Rauret et al. 1987) and particle size (Folk 1974). Sediments were digested by microwave system (MARS X CEM Co) for bulk metal analysis in two steps (Littau 1996): (1) 4 mL of HF, 4 mL of HNO_3 and 1 mL of HCl, all concentrated, were added to 0.3 g of sediment and heated to 175°C for 15 min and 200°C for 1 min; (2) 25 mL of 4% w/v H_3BO_3 solution were added and heated to 165°C for 15 min. The reactive fraction was extracted from the sediment by using HCl 1 M according to Huerta-Diaz and Morse (1990). Al, Cu, Cd, Pb and Zn concentrations were determined by flame atomic absorption spectrophotometry (VARIAN SpectrAA-220). Standard reference marine sediments (SRM-1646a: National Institute of Standards and Technology; and IAEA-356: International Atomic Energy Agency), as well as blanks were analyzed for bulk metal quality control purposes. Percent recovery means (n = 6) for SRM-1646a were: Cu = 94.2, Zn = 95.3 and Pb = 104.0. For IAEA-356 they were: Cd = 96.4, Cu = 96.5, Zn = 93.5, and Pb = 95.7. The metal concentrations varied less than 15%. Limits of detection (three times standard deviation of the blanks) for bulk metal analysis were: Cd = 0.097 µg/g, Cu = 0.093 µg/g, Pb = 0.262 µg/g, and Zn = 0.028 µg/g; and for analysis of bio-available fraction metal analysis they were: Cd = 0.015 µg/g, Cu = 0.010 µg/g, Pb = 0.190 µg/g, and Zn = 0.022 µg/g. Average concentrations were compared using one way ANOVA and Tukey multiple comparison tests using Statistical (version 6.0) software (StatSoft 1996). The enrichment factors (EF) for each metal were calculated using the formula (Soto-Jiménez and Páez-Osuna

2001): $EF = (M/Al)_{sample}/(M/Al)_{crust}$; where (M/Al) in the numerator is the metal concentration in relation to Al levels (µg/g dw) in sediment samples, and in the denominator is the average crust value taken from Martin and Maybeck (1979).

Results and Discussion

Table 1 shows the bulk averages of physical and chemical properties of surface sediments from the studied sites. Mud represented from 89.5% to 92.3% of the sediments, containing considerable amounts of carbonates and organic carbon. Low levels of carbonates and organic carbon ($p < 0.05$) were detected at site D during the rainy season, while higher values ($p < 0.05$) were found at sites B and D during the dry season. Organic carbon distribution is associated with mangrove forests and hydrodynamic factors, and its levels explain the black color and H_2S odor of the sediments.

No significant ($p > 0.05$) variations in bulk Cd and Pb concentrations at the studied sites were detected during either season (Cd varied from 3.1 to 3.3 µg/g and Pb varied from 49.6 to 54.0 µg/g). Ranges from 31.9 to 44.9 µg/g for Cu and from 217.8 to 323.5 µg/g for Zn were detected, with the highest ($p < 0.05$) values at sites B and C during the rainy season. All metal concentrations found are above those previously reported from the same sites in the lagoon (Osuna-López et al. 1986; Soto-Jiménez and Páez-Osuna 2001) but this increase is more evident in the cases of Cd and Zn. The increases can be explained by the accumulation of heavy metals from continued deposition from the surrounding area, which increases in the rainy season and is indicative of anthropogenic discharges and weathering. According to the mean quality guideline criteria for biological effects, sediments are above the level of low-range effects but below the level of median-range effects (Long et al. 1994).

The EF is an estimation of anthropogenic inputs of metals. In order to examine the behavior of heavy metals in the lagoon system, Fig. 2 presents the EF values of surface sediment sampled in 1983, 1994, and 2006 from the four sites. Similar EF trends for Cu and Pb were detected at all sites, with significant ($p < 0.05$) increases from 1983 to 1994 and a decrease from 1994 to 2006. EF for Zn increased significantly ($p < 0.05$) at all sites from 1983 to 1994; increments from 1994 to 2006 at sites A, B and C ($p < 0.05$ in sites B and C), while values at site D remained the same. Elevated EF values for Cd were detected at all sites in 2006, from 3 to 18 times higher than 1983 values, and from 1 to 2 times higher than those in 1994. According to Birth (2003), the EF in sediment samples from 2006 are interpreted as a minor enrichment of Cu (range = 1.3–1.9),
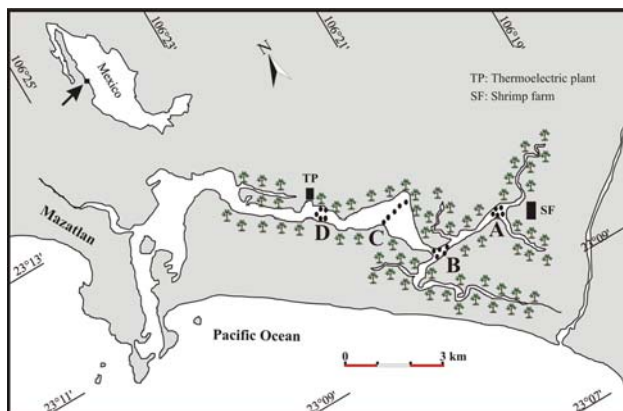

Fig. 1 Study area and localization of sampling sites

Table 1 Bulk average particle size, carbonates, organic matter and metals in surface sediments (n = 5 in each site)[1,2]

Site	% Mud	% CaCO3	% C Org	Cd	Cu	Pb	Zn
AI	90.1 ± 1.7[a]	5.0 ± 1.6[a]	4.3 ± 3.1[ab]	3.3 ± 0.1[a]	33.7 ± 5.1[a]	51.1 ± 6.8[a]	218.2 ± 12.1[a]
BI	89.5 ± 1.4[a]	8.5 ± 4.9[ab]	6.4 ± 3.0[b]	3.2 ± 0.1[a]	35.0 ± 4.8[ab]	51.6 ± 5.7[a]	274.6 ± 27.2[ab]
CI	90.0 ± 1.5[a]	7.8 ± 3.0[ab]	5.3 ± 3.6[ab]	3.3 ± 0.1[a]	35.8 ± 7.0[ab]	52.6 ± 6.0[a]	282.6 ± 38.1[ab]
DI	90.4 ± 2.2[a]	9.2 ± 5.0[b]	5.4 ± 1.6[ab]	3.1 ± 0.1[a]	31.9 ± 0.6[a]	54.0 ± 10.2[a]	217.8 ± 54.5[a]
AII	92.3 ± 1.4[a]	5.3 ± 1.2[ab]	6.2 ± 1.7[b]	3.1 ± 0.2[a]	33.9 ± 4.2[a]	51.8 ± 7.7[a]	240.9 ± 30.4[ab]
BII	90.0 ± 1.6[a]	7.2 ± 4.0[ab]	5.9 ± 0.8[b]	3.3 ± 0.1[a]	40.1 ± 3.9[ab]	49.6 ± 9.2[a]	304.9 ± 29.3[ab]
CII	90.5 ± 2.2[a]	5.3 ± 1.4[ab]	5.6 ± 2.7[b]	3.1 ± 0.2[a]	44.9 ± 4.9[b]	51.3 ± 7.4[a]	323.5 ± 75.4[b]
DII	90.4 ± 2.2[a]	4.9 ± 3.0[a]	2.8 ± 1.2[a]	3.2 ± 0.2[a]	32.8 ± 7.9[a]	50.2 ± 5.0[a]	245.2 ± 67.5[ab]

[1] Dry season sampling: AI, BI, CI and DI; rainy season sampling: AII, BII, CII and DII

[2] Different letter by column means significant differences ($p < 0.05$)

moderate enrichment of Pb (range = 4.2–5.1) and Zn (range = 2.3–3.7), and severe enrichment of Cd (range = 21.3–26.8). Enrichments of Pb in sediments are related to leaded gasoline emissions. The decreasing trend of Pb levels is consistent with the phase-out of leaded gasoline in México, completed in 1997 (Soto-Jiménez et al. 2006).

Because burning of fossil fuels is one of the major sources of Cd to environment (Phillips 1980), the EF for Cd are probable associated with use of fuels by fishing and merchant fleets, and with the thermoelectric plant on the edge of the study area. In addition, natural inputs of Cd associated with upwelling are possible in the Gulf of California (Sañudo-Wilhelmy and Flegal 1996).

Bio-available fraction represents the toxic potential of metal to biota. Their average distributions in each site during 1983, 1994, and 2006 are presented in Fig. 3.

Although different techniques among studies to extract it were used, values are comparable because represents the fraction of metal accessible to the biota (Tessier et al. 1979; Huerta-Diaz and Morse 1990). Because the reactive fraction comprises metal exchangeable, and the linked to carbonates and to oxy-hydroxides of Fe–Mn (Huerta-Diaz and Morse 1990), it is comparable to the first three bio-available fractions in the Tessier extraction scheme (Tessier et al. 1979). Bio-available Pb, Zn, and Cd increased from 1983 to 1994 but decreased by 2006 at most sites. In the present study, pattern ranges of bio-available metal were (µg/g): Zn (11.2–15.4) > Cu (9.4–11.1) > Pb (3.3–4.0) > Cd (0.46–0.51). In contrast, the percents of this fraction with respect to bulk metal had a different pattern: Cu (25.6%–33.4%) > Cd (13.8%–15.4%) > Pb (6.2%–7.8%) > Zn (4.6%–6.4%). Although enrichment was

Fig. 2 Heavy metals enrichment factors (EF) in surface sediments of sites of lagoon system in Mazatlán Harbor
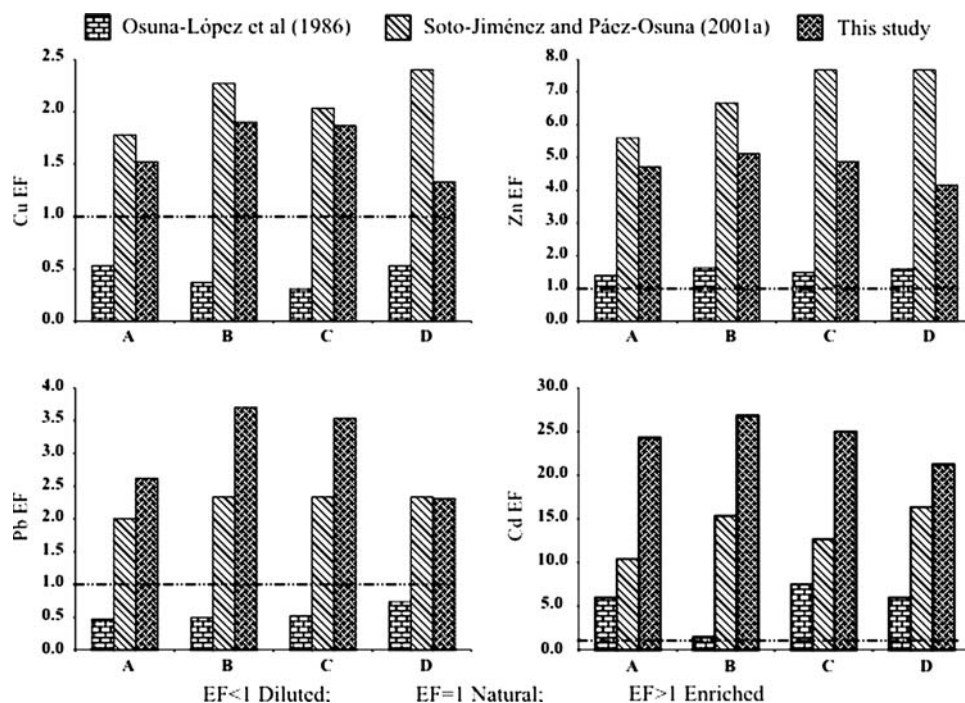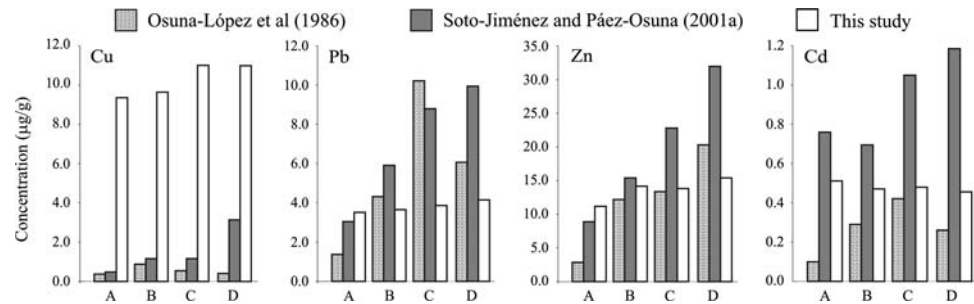
Fig. 3 Distribution of bioavailable heavy metals in sediments from sites in the lagoon system in Mazatlan Harbor

severe for Cd, most of the metal is linked to no-readily fractions, which may be associated with minerals produced in early diagenetic processes. The bio-available fraction of Cu was significantly ($p < 0.05$) higher in 2006, by at least four times the previous value, due to mobilization of this metal from the organic matter–sulfide phase, probably caused by oxidation of humic complexes and/or pyrite compounds. Sulfide minerals associated to fine sediment are considered as secondary sources of metals when reduced sediments are oxidized (Huerta-Diaz and Morse 1990). Mud sediments dominated all sites (Table 1) and oxidation could occur during sampling and extraction (Soto-Jiménez and Páez-Osuna 2001).

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